ARTICLE IN PRESS
CJCHE-00962; No of Pages 11
Chinese Journal of Chemical Engineering xxx (2017) xxx–xxx
Contents lists available at ScienceDirect
Chinese Journal of Chemical Engineering
journal homepage: www.elsevier.com/locate/CJChE

Energy, Resources and Environmental Technology

Thermodynamic behaviors of Cu in interaction with chlorine, sulfur, phosphorus and minerals during sewage sludge co-incineration☆

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ARTICLE INFO

Article history:
Received 5 September 2017
Received in revised form 4 October 2017
Accepted 9 October 2017
Available online xxxx

Keywords:
Sewage sludge
Incineration
Cupper
Thermodynamic equilibrium analysis

ABSTRACT

Thermodynamic equilibrium calculations were performed to reveal effects of interactions among Cl, S, P and other minerals on Cu migration. Our results showed that HCl(g), SO_2(g) and $(P_2O_5)_2$(g) were released from the sewage sludge co-incineration. Cl was found to weaken adsorption of Cu by Al_2O_3, CaO and Fe_2O_3, while S delayed reactions of Fe_2O_3 and Al_2O_3 with Cu, with P having no effect on reactions between the minerals and Cu. Among the coupled systems of Cl, S and P, the co-existences of Cl and S, and Cl, S and P were determined to inhibit Cu volatilization, and the co-existence of Cl and P had an enhancing effect. Cu migration was affected only by S in the S and P system. With the SiO_2, CaO and Al_2O_3 system, both Cl alone and Cl and P led to failed reactions between the minerals and Cu. In the systems of S, S and Cl, S and P, and S, Cl and P, the migration behavior of Cu was mainly affected by S at low temperatures and by Cl at high temperatures, whereas P had no effect on Cu migration during the entire process.

1. Introduction

In response to increasingly growing human population, there has been a paralleling increase in the standards applied for wastewater discharge, the wide spread development of wastewater treatment plants and technologies, and the quantity of sewage sludge as a byproduct of wastewater treatment plants. Properties of sewage sludge such as high moisture content, huge volume, bad odor, toxic and harmful substances, and ease of degradation pose significant public health risks [1,2]. Given the recent treatment and pollution control technologies and policies, (co-)incineration of municipal sewage sludge has been considered to be one of the most feasible options for its disposal. Co-incineration with coal may be applied to reduce investment costs and environmentally harmful wastes as well as to enhance resource recovery, reuse and recycling [3]. However, sewage sludge may also increase emissions of inorganic and organic air pollutants during the co-incineration due to its heavy metal (HM) content, thus restricting the development of environmentally benign co-combustion technologies [4].

Copper (Cu) concentration of sewage sludge may vary greatly with sources, locations, and time. For example, the mean Cu concentration was estimated at (63.7 ± 72) $mg\cdot kg^{-1}$ for commercial composts with 2.6% sewage sludge in China [5], (95.8 ± 157) $mg\cdot kg^{-1}$ for soils amended with sewage sludge in Turkey [6], and 410 $mg\cdot kg^{-1}$ for sewage sludge in Sweden [7]. The previous studies reported 182.5 $mg\cdot kg^{-1}$ to be the mean Cu concentration of sewage sludge in China [8]. According to the guideline of *Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant* (GB18918-2002), this exceeded the pollutant limit values of agricultural sludge applications for basic and acid soils by 2.3% and 7.1%, respectively. Sludge as a large source of phosphorus (P), chlorine (Cl)-containing flocculants in wastewater treatment, Cl-containing conditioners in deep dewatering of sludge, and sulfur (S)-containing fire coals add further P, Cl, and S to the co-incineration systems [9,10]. Therefore, Cl, S and P interact with Cu in the sludge-oriented co-incineration systems. In addition, the main slag components of the sludge/waste/coal co-incineration include SiO_2, Al_2O_3, and CaO which in turn allow for adsorption of heavy metals in different forms [11]. These minerals precipitate in the competing reactions between HMs and Cl, S, and P during co-incineration, thus changing the migration and transformation paths of HMs including Cu [12]. To the best of our knowledge, there exist no studies on migration and

☆ Supported by the Science and Technology Planning Project of Guangdong Province, China (2017A050501036; 2015B020235013; 2015A020215033; 2017B090907012), the Scientific and Technological Planning Project of Guangzhou, China (201620160403005 8; 201704030109), and Guangdong Special Support Program for Training High Level Talents (2014TQ01Z248).
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https://doi.org/10.1016/j.cjche.2017.10.019
1004-9541/

Please cite this article as: J. Liu, *et al.*, Thermodynamic behaviors of Cu in interaction with chlorine, sulfur, phosphorus and minerals during sewage sludge co-incineration, *Chin. J. Chem. Eng.* (2017), https://doi.org/10.1016/j.cjche.2017.10.019

transformation behavior of Cu when coupled with interactions between Cl, S, and P and the minerals such as SiO_2, Al_2O_3 and CaO.

The multiple migration pathways of HMs during sludge co-incineration are a function of incinerator types, their operation variables (*e.g.* incineration temperature, residence time, and combustion atmosphere) [13,14], initial sludge compositions, and Cl and/or S contents of mixed wastes [15,16]. Cl-containing compounds can react with Cu easily, thus forming metal chlorides and Cu emissions in large quantities [17,18]. At low temperatures, metal sulfides can substitute metal chlorines or metal oxides, thus inhibiting Cu volatilization. However, at temperatures above 800 °C, the presence of volatile metal sulfides makes S compounds enhance Cu volatilization [19]. During the co-incineration, P-containing compounds can form phosphate compounds with strong heat stability, thus inhibiting Cu volatilization and emission [20,21]. In the complex sludge co-incineration systems coupled with Cl, S, and P, Cu migration and transformation are affected by both the form of Cu and the competing reaction between Cl and S. This reaction is also influenced by the existence and forms of P and the minerals. However, there still exist gaps in the current knowledge accumulation about the roles and relative contributions of P and the minerals in these reactions.

Currently, the simulated grate, and fluidized bed incinerators are usually employed to track the migration and transformation behaviors of HMs in the laboratory [22–29]. Thus far, due to the limitations of the partial detection technologies, the migration and transformation behaviors of Cu across the entire range of temperatures during sludge co-incineration have not been obtained accurately using experiments under various interaction conditions. In addition, Cu compounds act during the co-incineration as the catalysts in the formation of PCDD/Fs at low temperatures ranging from 300 °C to 500 °C, under the presence of Cl [30]. As an important catalyst for the generation of dioxins and Cl source, $CuCl_2$ is more active than KCl, $CaCl_2$ and $FeCl_3$ [31]. In addition, a previous incineration experiment showed that when 0.07% $CuCl_2 \cdot H_2O$ was added to simulated waste, the PCDD/Fs production increased by 30% [30]. Therefore, it is necessary to accurately estimate and monitor chemical interactions among Cl, S, P, and Cu across the entire temperature range and process.

In so doing, the present study predicts the thermal conversion behavior of Cu in interaction with Cl, S, and P using the thermodynamic equilibrium software (FACT sage 6.3). Also, this study quantifies effects of the coupling of Cl, S, and P with the minerals of SiO_2, CaO, and Al_2O_3 on migration and thermodynamic equilibrium behaviors of Cu. This can in turn pave the way for effective predictions of Cu emission, thus hindering the formation of dioxins during sludge co-incineration.

2. Materials and Methods

2.1. Sampling strategy

Sewage sludge used in the experiments were sampled from four large sewage treatment plants in Guangzhou named KFQ, DTS, LJ, and LD whose specific properties were listed in Table 1 [32,33]. DTS, LJ, and LD are the sewage treatment plants on a larger scale that adopt the conventional active biomass sludge treatment technology, and thus, are representative of the typical sludge and plant characteristics. Their sludge treatment capacity accounts for over 60% of the total sewage treatment capacity in Guangzhou. To compare municipal sewage sludge composition in detail, sludge samples from a Guangzhou paper mill (ZZ) and a sewage treatment plant (ZQ) in the city of Zhaoqing were also collected.

Elemental C, N, H, O and S contents of sludge samples were detected using an elemental analyzer (Elementar Vario EL III, Germany). While Cl content was determined using the methods of water leaching and nitrate titration, mineral contents (SiO_2, CaO, Al_2O_3, and Fe_2O_3) were measured using an X ray fluorescence spectrometer (Rigaku 100e, Japan). All results are shown in Table 2 [32,33].

Table 2
Composition of elements and minerals in sewage sludge (%) [32,33]

Sludge	N	C	H	O	S	Cl	SiO_2	CaO	Al_2O_3	Fe_2O_3
ZZ	1.15	22.98	3.20	23.57	0.88	0.35	21.32	18.13	8.75	0.37
DTS	4.70	30.30	4.01	21.46	2.15	0.36	30.14	3.96	7.53	1.94
LJ	4.56	25.95	4.29	19.17	1.68	0.50	35.41	2.82	6.73	2.06
KFQ	4.48	33.73	5.25	22.98	2.55	0.21	28.41	3.71	4.14	2.19
LD	2.88	17.46	3.51	16.14	1.22	0.21	37.16	3.21	9.16	2.27
ZQ	6.09	34.04	5.03	23.48	1.61	0.50	/	/	/	/
Average value	3.98	27.41	4.21	21.13	1.68	0.35	30.49	6.37	7.26	1.77

To accurately reflect the HM contents of the municipal sludge samples in China, this study used their time-series data from 2006 to 2013 and estimated the geometric average value of Cu content as the initial value during the simulation, as can be seen in Table 3 [8].

Table 3
Concentration of Cu in sewage sludge in China [8]

Heavy metal	Sample size	Content range/mg·kg^{-1}	Geometric average value/mg·kg^{-1}	Arithmetical average value/mg·kg^{-1}
Cu	84	55.7–2867.4	182.5	283.5

2.2. Thermodynamic method

The equilibrium constant method and the Gibbs minimum free energy method are usually employed to deal with the chemical equilibrium of complex systems. The FACT sage 6.3 software applied in this study is based on the Gibbs minimum free energy method. The composition and concentration of each component were obtained under isothermal and isobaric conditions, taking the Gibbs free energy minimization as the equilibrium criterion, and using the Lagrange undetermined coefficient method. In this study, it is assumed that air, sludge and other original reaction substances are added into the sludge co-incineration system at a certain temperature and pressure for complex chemical reactions to occur. When the system reaches equilibrium, the Gibbs free energy of the entire system reaches the minimum. In this way, the composition and concentration of various gaseous substances and solid materials within the system can be estimated (Fig. 1).

The equilibrium system used in predicting the speciation and concentration of Cu in the sludge co-incineration system is a simple system in which the sludge samples were assumed to only contain the major elements (C, H, O, N, S, and Cl) and the minerals, while the flue gas is

Table 1
Description of wastewater treatment plant (WWTP) [32,33]

Sewage plant	Treatment scale/m^3·d^{-1}	Service area/km^2	Service population	Processing technology	Sludge treatment method	Proportion of industrial wastewater
KFQ	3.0×10^4	9.6	6.0×10^4	Active sludge	Landfill	70%
DTS	60.66×10^4	89.7	142.7×10^4	Active sludge	Landfill	40%
LJ	40.0×10^4	124.5	134.3×10^4	A^2/O	Building material	<5%
LD	103.67×10^4	158	225.8×10^4	Active sludge	Building material	<5%

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